

DRAWINGS ATTACHED.

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COMPLETE SPECIFICATION.

Improvements in or relating to the Manufacture of Graphite.

We, UNITED KINGDOM ATOMIC ENERGY
AUTHORITY, London, a British Authority,
do hereby declare the invention, for which
we pray that a patent may be granted to us,
and the method by which it is to be per-
formed, to be particularly described in and
by the following statement:—

The present invention relates to the manu-
facture of graphite.

Graphite has been proposed as a canning
material for the nuclear fuel of nuclear re-
actors and in this connection it will be known
that fission product containment is one of
the problems to be solved in reactor design
and one solution to this problem is to use
highly impermeable graphite. A distinction
must be made between the factors perme-
ability, porosity and density, for much pre-
vious work has been done to produce very
dense graphite. It has not so far been pos-
sible to produce graphite having no pores,
but comparatively little attention has been
directed to producing minimum permeability
as opposed to the attempt to product maxi-
mum density. When the graphite has been
produced, it is known that a proportion at
least of the open pores may be closed by
various impregnation and similar treatments.

It has been found that in fact to achieve
the high standard of impermeability required
for nuclear fuel containers, the manufactur-
ing process which gives a most consistent
high standard is extrusion. Hitherto graphite
stock has been manufactured from ingredi-
ents which include coke as a starting ma-
terial and has been highly porous and not
amenable to the production of low perme-
ability artefacts.

[Price 4s. 6d.]

An object of the invention is to produce
an extrudable graphite material capable of
yielding a highly impermeable article.

According to the present invention, there
is provided a method of manufacturing arti-
ficial graphite which comprises the steps of
preparing a three-component grist, admixing
said grist with a carbonisable binder to form
a green compact, carbonising such green
compact to form a carbon compact and
graphitising such carbon compact, wherein
said three component grist comprises a first
component of coarse artificial graphite, of
particle size substantially in the range 50—
250 microns, 10—30% by weight of a second
component of fine artificial graphite of par-
ticle size less than 25 microns, and 25—40%
by weight of a third component of carbon black.

It has been found moreover that furfuryl
alcohol is a most satisfactory impregnant for
further increasing the impermeability of the
extruded and graphitised article and that it
may subsequently be thermally decomposed
to produce carbon in the pores. However,
in order to achieve satisfactory impregnation
it is believed that the ideal material should
have its open pores in the region of 0.8 to
0.6 microns diameter.

It is, therefore, a further object of the
present invention to produce an artificial
graphite having its open pores as far as pos-
sible in the region 0.8 to 0.6 microns dia-
meter. It is advantageous if the proportion
of open pores is low, as this reduces the
degree of impregnation necessary, and it is
also advantageous if total porosity is as low
as possible, as the material is then stronger

and more homogeneous, but these are both secondary considerations.

Such a material may be used for other purposes beside those outlined for its relatively high density is allied to good machinability together with high compressive and tensile strengths. Thus, for example, such a graphite may be used for plungers and dies, or proton beam stops, to replace coarser grained graphites where a minimum of adsorbed gases are necessary, and even for lining rocket nozzles.

The preferred ratio of total graphite to carbon black may be between 75:25 and 60:40 by weight.

The proportion of fine artificial graphite in the total grist may be from 10 to 30% by weight, but is preferably 18 to 25% by weight.

The addition of a portion of fine carbon black (mean particle size 0.2 microns) does not appear to affect the mean pore diameter, but it may be desirable as the final product may be rather more dense due to a reduction of the total number of open and closed pores.

The coarse graphite should preferably all be smaller than 60 mesh B.S.S., but the size used depends on the extrusion die diameter. Typical sieve analysis of the coarse artificial graphite may be:—

	By weight
Between 60 and 120 mesh B.S.S.	34%
" 120 and 300 "	46%
Smaller than 300 "	20%

The coarse artificial graphite may be sized, as a specific example, as follows:—

Size (microns)	% by weight undersize
251	100
124	66
53	20
40	13.8
30	9.6
20	5.7
10	2.2
5	0.4

A more restricted size range for the coarse artificial graphite is substantially entirely within the size range 50—100 microns diameter and the restricted range is preferred.

A similar size tabulation for the fine artificial graphite is as follows:—

Size (microns)	% by weight undersize
25	100
20	92
18	88.9
16	87.5
14	79.5
12	69.5
10	53.0

Size (microns)	% by weight undersize
8	38.5
6	22.6
5	15.7
4	7.9

Preferably substantially all the fine artificial graphite is within the range 5—20 microns.

The preferred carbon black has a particle size of 0.4 micron and the preferred fine carbon black (optional) has a particle size of 0.02 micron.

It will be apparent that due to the proportion of carbon black in the grist, the resultant fine grained graphite will not be wholly graphitised but this appears to be unavoidable since at the present time it does not appear to be possible to obtain a nuclear grade graphitisable component of the required particle size.

The preferred ratio of the components by weights in the grist is:—

Coarse artificial graphite	42%
Fine artificial graphite	18%
Carbon black	40%

In order that the invention may more readily be understood, two embodiments of the same will now be described by way of examples.

EXAMPLE 1.

A grist was prepared containing the three components, namely fine artificial graphite 20%, coarse artificial graphite 46.7%, and carbon black 33.3% by weight, and this grist was thoroughly mixed. Then a proportion of finely sieved binder is added and successively cold and hot mixed. The preferred binder is a coal tar pitch (softening point 80° C.) and is desirably used in proportions of 20 to 26% by weight of the total, the lowest satisfactory proportions being desirable as otherwise there is a risk of blow holes on carbonisation of the binder.

The hot mix is now transferred to the heated chamber of a vacuum extrusion press, evacuated and tamped for some 3 minutes at a pressure of 100 tons, the chamber being heated to 120° C. The mix is then extruded through a die at 120° C. to provide 2" diameter green compacts which are allowed to cool.

The green compacts are individually packed in metal tubes and the space between the compact and tube filled with a coarse coke packing grist and the tubes are heated in a furnace under a constant gas pressure of about 100 p.s.i. The carbonising step is conducted at a temperature of about 900° C., heating being effected slowly as is conventional. It may be more convenient to heat in two stages, the rates of heating then being as follows:—

STAGE I.

20—200° C. at 6° C./hr.
 300—500° C. at 3° C./hr.
 500—550° C. at 6° C./hr.
 held at 550° C. for 4 hrs.

STAGE II.

20—500° C. at 20° C./hr.
 500—650° C. at 6° C./hr.
 650—900° C. at 10° C./hr.
 held at 900° C. for 4 hrs.

After cooling, the carbon compacts are graphitised at a temperature of 2700° C., taking approximately nine hours to reach this temperature. The carbonising and graphitising steps are, of course, carried out in an inert or non-oxidising atmosphere.

EXAMPLE 2.

The components of the grist are fine artificial graphite 18%, coarse artificial graphite 42% and carbon black 40% by weight and these are thoroughly mixed. An addition is then made of a binder, conveniently coal tar pitch, which may be added at the rate of 20 to 26% by weight of the total, the minimum of binder being used which will provide satisfactory extrusion under the conditions of operation. It is well known that the minimum of binder is desirable as, on heating, pitch melts and releases volatile components.

After thoroughly mixing cold, the mixture is transferred to a hot mixer and then transferred to a hot extrusion press where, after evacuation to remove entrained gases, the mixer is extruded through a 2" diameter die at the rate of 1 foot per minute and at a temperature of 120° C. The green compacts after being allowed to cool are individually packed into metal tubes, the space between the compact and the tube (approximately $\frac{3}{16}$ " being filled with a medium size coke packing grist to support the green compact during heating.

The heating is effected under a constant pneumatic pressure of 100 p.s.i.g. in a reducing or neutral atmosphere and the rate of heating is slow up to a temperature of 550° C. A convenient rate for the heating is 3° C. per hour. During this heating step, the pitch binder liquefies and is then carbonised whilst volatiles escape and we have found that close control is necessary in order to reduce the number of compacts which are cracked or otherwise defective. However, this a well known difficulty in the preparation of graphite articles of this nature and must be solved for each specific grist, mix, size of particles and oven.

Having been heated at 550° C. and held at this temperature for a period of about 4 hours, the compacts are allowed to cool and

may then be removed from the supporting tubes if desired, although this step is not necessary.

Thereafter the compacts are heated at atmospheric pressure to a temperature of 900° C. and are maintained at this temperature for a further period of about 4 hours to produce a fully carbonised compact. These fully carbonised compacts, after cooling, are extremely hard and may be removed from the supporting tubes and may then be reheated to a temperature in the region of 2700° C. to graphitise the compacts. It is only necessary to hold the compacts at this temperature for a time of the order of 30 minutes.

A specimen of graphite produced by the above described process was examined and was found to have a permeability constant of 9.6×10^{-13} cm² (viscous or "slip" flow) and 5.8×10^{-8} cm (Knudsen flow as defined in Chapter III of "Flow of Gases through porous media", P. C. Carman, 1956), giving an overall permeability coefficient of 10^{-2} cm²/sec. for helium at atmospheric pressure.

The attached drawings illustrate the physical properties of the graphitised compacts, wherein:—

Fig. 1 shows pore size vs. porosity for certain compacts.

Fig. 2 shows the same factors for other compacts.

Fig. 3 shows the same factors for the compact of Example 1.

Fig. 4 shows the same factors for the compact of Example 2.

As explained above the important feature to be achieved is that the pore size should be in the range 0.8 to 0.6 micron. Fig. 1 shows curves for four compositions A, B, C and D, all these compositions containing 66.7% by weight total graphite. The pore size is measured using mercury at pressures up to 15,000 p.s.i. and obviously this measures the pore entrance size which is plotted against porosity which is expressed as "internal volume as percentage of bulk volume".

In Fig. 1, the curves correspond to the following compositions, with the total graphite constant:—

Curve	Fine graphite percentage
A	0
B	5
C	10
D	15

Fig. 2 shows the effect of varying the total graphite content as follows:—

Curve	Total graphite percentage	Fine graphite percentage
D	66.7	15
E	60	13.5
F	70	15.75

Fig. 3 shows a curve that is obtained for the composition of Example 1, namely fine graphite 20%, coarse graphite 46.7%, carbon black 33.3% by weight.

As the proportion of fine graphite is increased above 30% by weight the slope of the curves falls off and increased porosity is apparent.

Finally Fig. 4 shows the curve that is obtained by the composition of Example 2, viz: fine graphite 18%, coarse graphite 42% and carbon black 40% by weight.

Tubes of this material having a wall thickness of $\frac{1}{4}$ " were twice impregnated with furfuryl alcohol under a previously proposed procedure as described in U.K. Patent No. 901,847 and were then submitted to a final heat treatment at 2000° C. in argon at atmospheric pressure. It was found that the impregnation was effected satisfactorily and the overall final permeability to krypton at room temperature was found to be 10^{-7} cm²/sec.

It is interesting to quote densities and porosities for the graphite as follows:—

	Graphite	Density (gms/cm ³)	Cumulative porosity
Curve	A	1.920	0.104
	B	1.917	0.103
	C	1.907	0.107
	D	1.871	0.120
	E	1.921	0.099
	F	1.855	0.135

These figures emphasise the fact that pore size distribution, porosity and density are not necessarily interlinked.

WHAT WE CLAIM IS:—

1. A method of manufacturing artificial

graphite which comprises the steps of preparing a three-component grist, admixing said grist with a carbonisable binder to form a green compact, carbonising such green compact to form a carbon compact and graphitising such carbon compact, wherein said three component grist comprises a first component of coarse artificial graphite of particle size substantially in the range 50—250 microns, 10—30% by weight of a second component of fine artificial graphite of particle size less than 25 microns and 25—40% by weight of a third component of carbon black.

2. A method of manufacturing artificial graphite according to Claim 1 in which the components of the grist by weight are in the following proportions: coarse artificial graphite 42%, fine artificial graphite 18% and carbon black 40%.

3. A method of manufacturing artificial graphite according to Claim 1 or Claim 2 in which the particle size range of the coarse artificial graphite is from 50 to 100 microns, that of the fine artificial graphite from 5 to 20 microns and the particle size of the carbon black substantially 0.4 microns.

4. A method of manufacturing artificial graphite according to Claim 3 in which the grist includes a proportion of fine carbon black having a mean particle size of 0.02 microns.

5. An article of artificial graphite manufactured according to Claim 1 or Claim 2 and having open pores in the size range 0.8 to 0.6 microns.

6. An article of artificial graphite manufactured according to the method described in relation to Example 1.

7. An article of artificial graphite manufactured according to the method described in relation to Example 2.

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Chartered Patent Agent,
Agent for Applicants.

FIG.1.

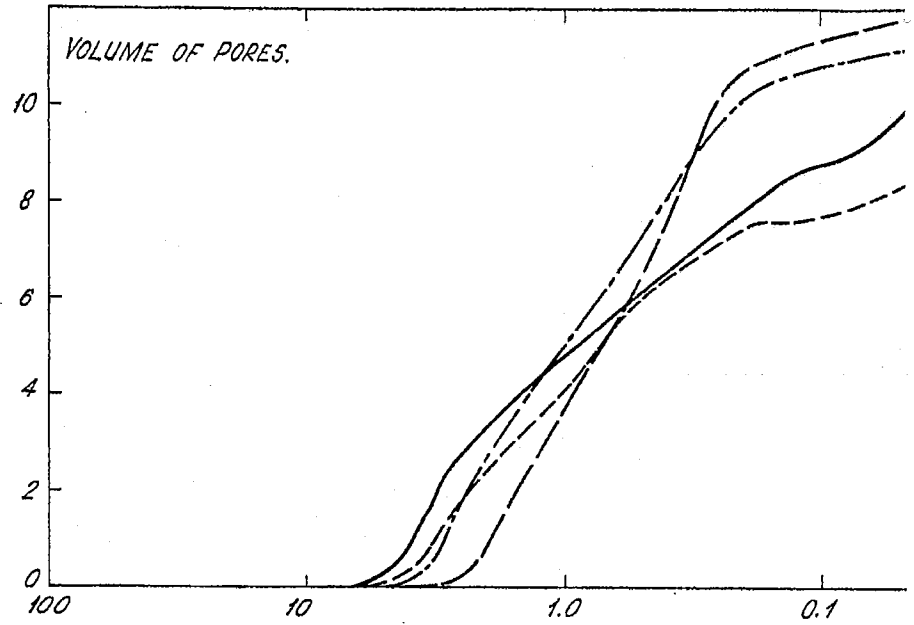
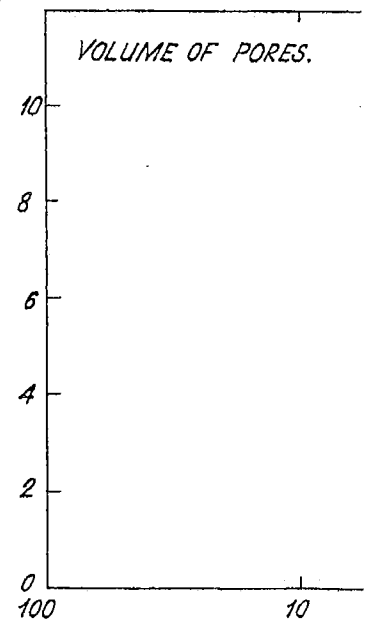


FIG.2.



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COMPLETE SPECIFICATION

2 SHEETS

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the Original on a reduced scale
Sheet 1

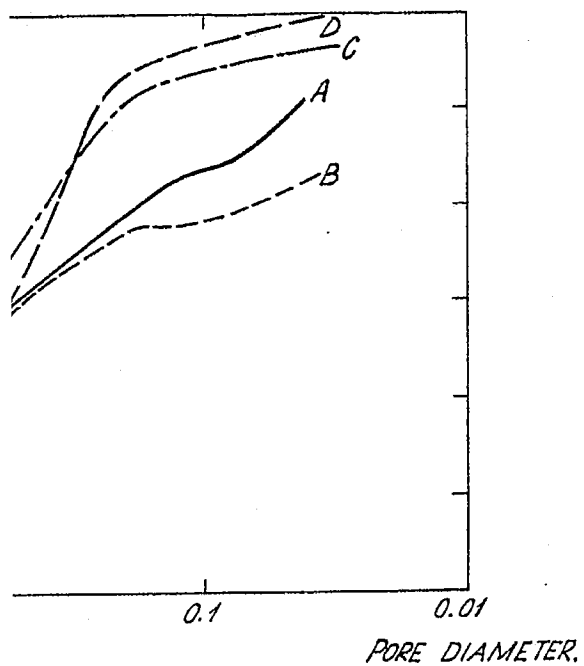
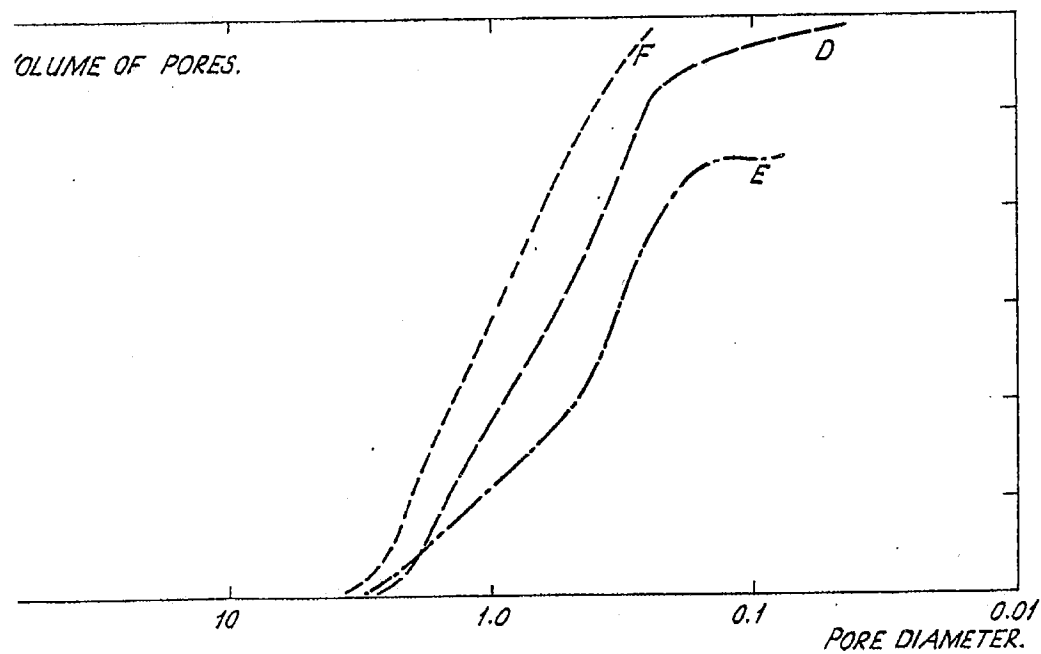


FIG.2.



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COMPLETE SPECIFICATION
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2 SHEETS
Sheet 1

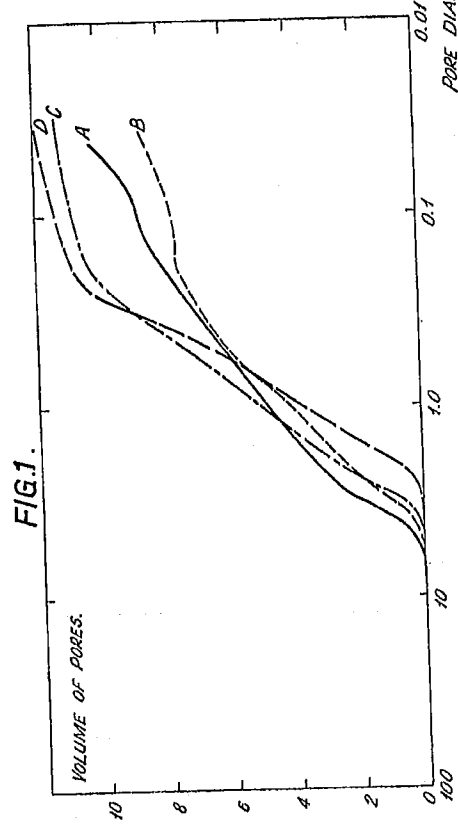
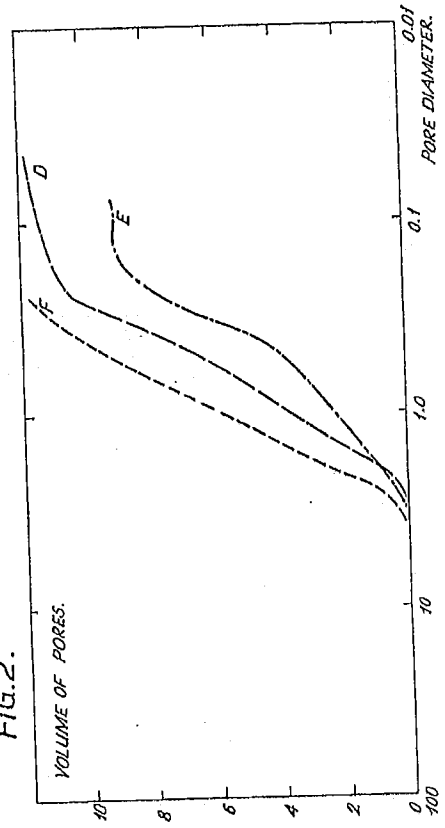


FIG.2.



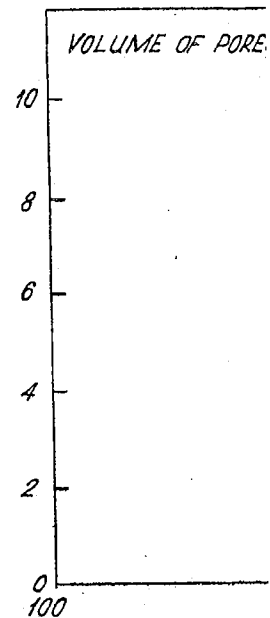


FIG.4.

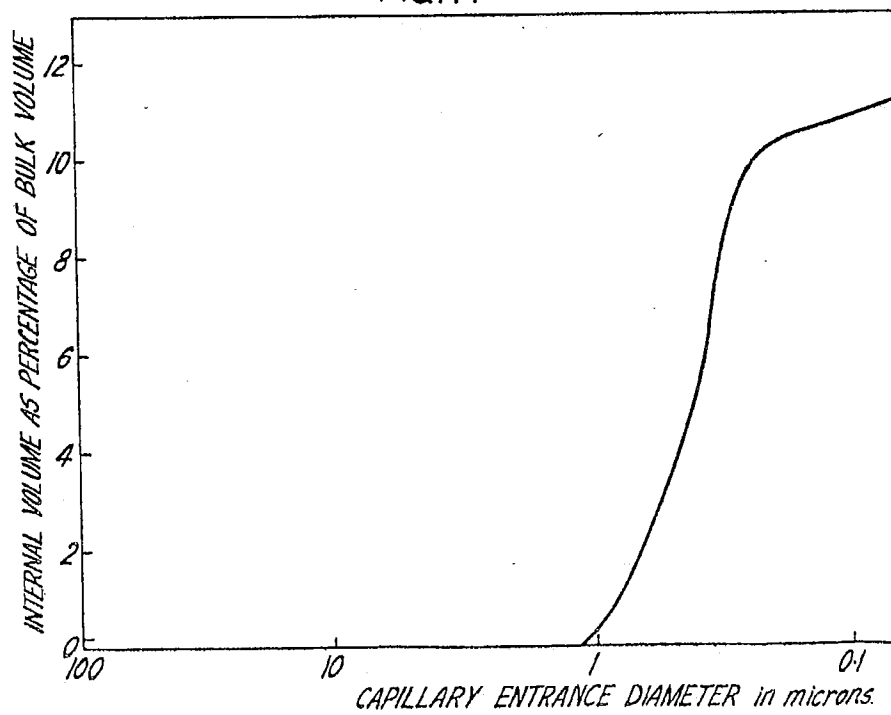


FIG.3.

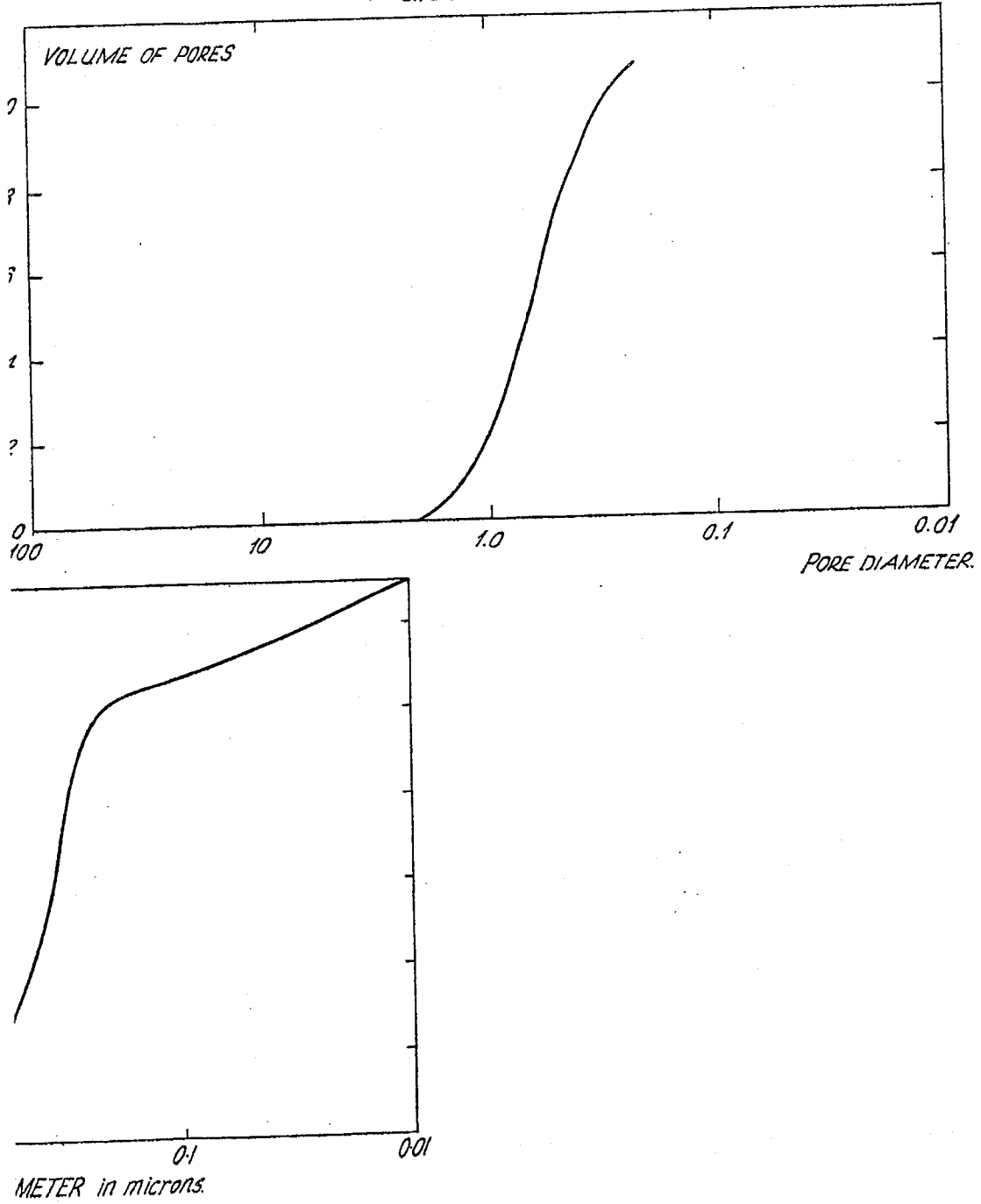


FIG.3.

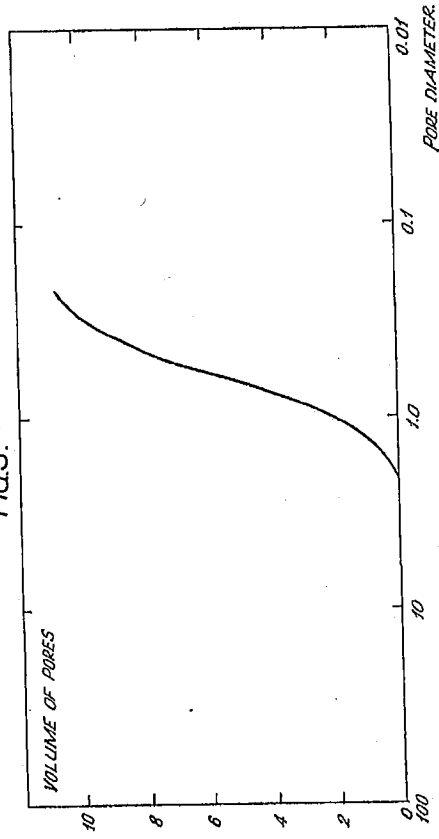


FIG.4.

